

Efficient Host Material Containing 1,3,5-Triazine Moiety for Red Phosphorescent Organic light-emitting diodes (OLEDs)

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Received August 5, 2011, Accepted September 14, 2011

Key Words : Triazine, Host, Red phosphorescence, OLEDs

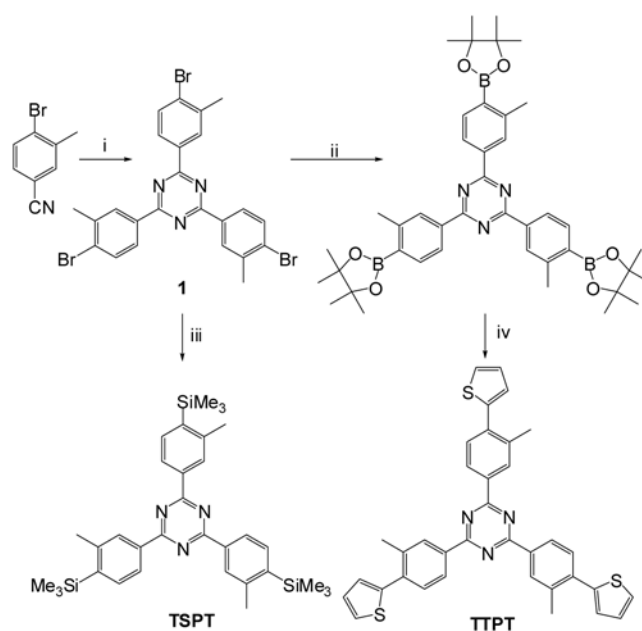
Organic light-emitting diodes (OLEDs) using organic fluorescent dyes as emitting materials have multilayered structure of the following order in general: cathode/hole injection layer/hole transporting layer/emissive layer/electron-transporting layer/electron-injection layer/anode.¹ The internal quantum efficiency of fluorescent dye, however, is limited up to 25% maximum because of the singlet exciton it utilizes.² Phosphorescent organic light-emitting diodes have also received a great deal of attention because of their high internal efficiency (nearly 100%) from the utilization of both singlet and triplet excitons.³ In spite of a number of advantages in phosphorescence organic light-emitting diodes (PHOLEDs), several drawbacks still remain, most notably is concentration quenching of the emitter.⁴ Host-embedded phosphorescent emitters are generally used to avoid this defect. Additionally, energy transfer between host and dopant molecule is used in PHOLEDs to achieve high efficiency.⁵ Therefore, the development of suitable host materials in accordance with a dopant is considered major issue because the emission in the emissive layer depends on the energy matching of the host and guest molecule.

Recently, a few report have demonstrated that triazine based heterocycles with bipolar character showed high efficiency in OLEDs performance.⁷ However, the number of triazine derivatives with bipolar character is very limited,^{4,7} therefore, there is still a strong need for the development of triazine based compounds. Our interest focuses on the development of efficient host materials based on triazine because of their unique thermal and optical properties. During our ongoing efforts on the development of luminescent materials and host for PHOLEDs,⁸ we have found that triazine based molecules, such as 2,4,6-tris(3-methyl-4-(thiophen-2-yl)phenyl)-1,3,5-triazine (TTPT) and 2,4,6-tris(3-methyl-4-(trimethylsilyl)phenyl)-1,3,5-triazine (TSPT) exhibit good glass-forming nature, low-lying HOMO energy and unique optical/electrochemical behaviors as compared to those of other triazine derivatives.⁴ Based on these facts, we envisioned that these molecules would potentially be good hosts for red guest in PHOLEDs. The facts have also prompted us to investigate electroluminescent (EL) characteristics of these materials. We herein report the

synthesis, characterization and OLED performance of triazine-based compounds.

Result and Discussion

Starting material **1** was synthesized by a slight modification of a previous synthetic methodology reported by Kostas *et al.*, as shown in Scheme 1. (See experimental section)⁷ By cyclotrimerization of 4-bromo-3-methylbenzonitrile with trifluoromethanesulfonic acid in dry chloroform, compound **1** was obtained in a high yield. TTPT was then synthesized using a Suzuki coupling by the reaction of 2-bromothiophene with 2,4,6-tris(3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine and was obtained in good yields (~85%). All compounds were fully characterized by varied spectroscopic methods.



Scheme 1. Synthetic routes of TSPT and TTPT: i) CF₃SO₃H/CHCl₃, 0 °C~RT, 24 h. ii) *n*-BuLi/THF, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, RT, 24 h. iii) *n*-BuLi/THF, Me₃SiCl, 0 °C~RT, overnight. iv) 2-bromothiophene, 2 M Na₂CO₃, Pd(PPh₃)₄, THF, reflux, overnight.

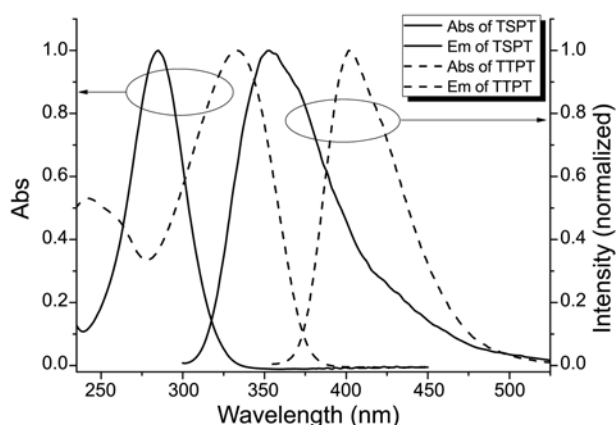


Figure 1. Absorption and emission spectra of **TSPT** and **TTPT** in CH_2Cl_2 at room temperature.

Organic compounds often used as host in OLEDs should have high triplet energy, thermal stability and good film-forming ability due to the need of effective energy transfer from host to dopant and the occurrence of joule heat during device operation.^{8,9} Therefore, we have investigated thermal and photophysical characteristics of both **TSPT** and **TTPT**. The UV/vis absorption and photoluminescence (PL) emission spectra of **TSPT** and **TTPT** in dilute CH_2Cl_2 solutions are depicted in Figure 1.

The UV/vis spectrum of **TSPT** exhibits absorption band centered at 285 nm, while **TTPT** shows a red-shifted intense absorption with $\lambda_{\text{max}} = 334 \text{ nm}$ ($\epsilon > 90,000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) between 250 nm and 400 nm. A remarkable red-shifted absorption of **TTPT** relative to that of **TSPT** can be attributed to the lengthening of conjugated system with the addition of a thiophene ring to triazine core. The electronic transition observed for **TSPT** is mostly attributed to a triazine and phenyl ring $\pi\text{-}\pi^*$ transition, while phenylthiophene to triazine $\pi\text{-}\pi^*$ transition is observed in **TTPT**. As shown in Figure 2, the HOMO levels of **TTPT** is mainly occupied by π orbitals with dominating contributions from thiophene and phenyl groups whereas the LUMO level is largely dominated by π^* orbital contributions from triazine ring. This theoretical calculation is in accordance with the experimental observation. **TSPT** and **TTPT** emit violet and blue light with maximum emissions at 352 nm and at 401 nm respectively, when irradiated by UV light. Compared to the PL quantum yield ($\Phi_{\text{PL}} = 95\%$) of 9,10-diphenylanthracene (DPA), compounds **TSPT** and **TTPT** show values of 0.01% and 10%, respectively.

The thermal properties of **TSPT** and **TTPT** were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (See supporting information). A weight loss of 2% ($T_{2\%}$) and 5% ($T_{5\%}$) in **TSPT** are observed at 248 °C and 321 °C, respectively, while $T_{2\%}$ and $T_{5\%}$ are observed at 289 °C and 350 °C in **TTPT** respectively. These observations indicate that **TTPT** has higher thermal stability than **TSPT**. The glass transitions of the two compounds were not observed during either the first or second heating cycle. Only melting transitions were observed at 200 °C for

TSPT and 280 °C for **TTPT**, respectively. **TTPT** showed consistent and fully reproducible DSC diagrams during two cycles of heating and cooling, indicating that this compound is thermally stable up to their melting points. Reproducible DSC diagrams during the two cycles were not observed in **TSPT**. In view of this thermal stability, **TTPT** is a more suitable candidate for use in OLEDs than **TSPT**. Thus, we have systematically investigated the electrochemical behavior and OLEDs performance of only **TTPT**.

To investigate the electrochemical behavior of **TTPT**, cyclic voltammetry experiments were carried out using ferrocene (Fc/Fc^+) as the internal standard. Due to the limited range available in CH_2Cl_2 , and inability of our instrument to measure reliable reduction potentials in the region of -2.0 to -3.5 V , we have obtained reliable oxidation potentials only. Upon the anodic sweep in a mixture of CH_2Cl_2 and CH_3CN , irreversible oxidations are observed. (see supporting information) The onset potentials of oxidation appeared at 1.78 V (*vs* Ag/AgCl), correspondent to 1.34 V (*vs* Fc/Fc^+). Based on these observations, the HOMO level was estimated using the oxidation potential of ferrocene/ferrocenium (4.8 eV below the vacuum level),¹⁰ and as a result estimated HOMO level of 6.14 eV has been obtained. This value is lower than that of 2-(4-(3,6-dimethylcarbazol-9-yl)-phenoxy)-bis-4,6-biscarbazolyl-1,3,5-triazine (5.48 eV) but is higher than that of 2,4-diphenyl-6-(49-triphenylsilanylbi-phenyl-4-yl)-1,3,5-triazine (6.5 eV). In addition this value is very close to that of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), which is commonly used as a hole-

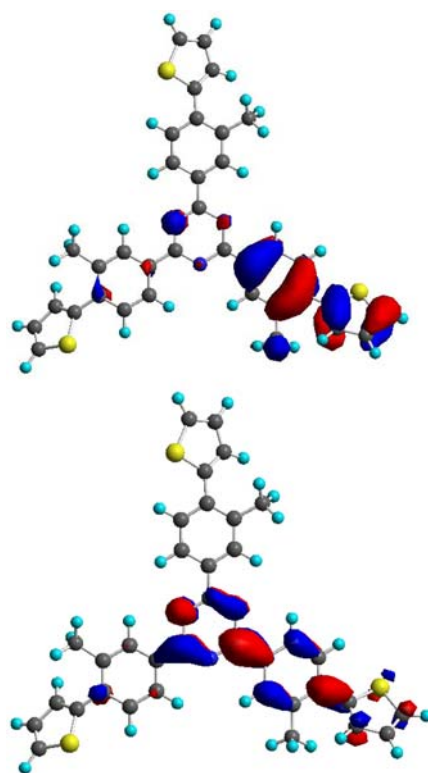


Figure 2. Isodensity surface plots of the HOMO(left) and LUMO(right) of **TTPT**.

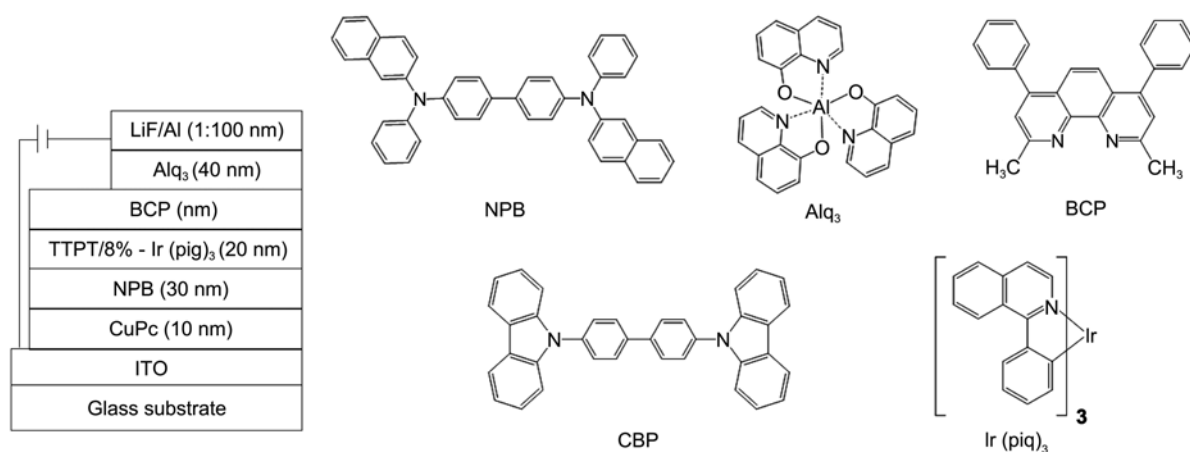


Figure 3. Device structure and molecular structures used in this study.

blocking material in PHOLEDs. Therefore, further research on the hole-blocking characteristics of **TTPT** is needed. The LUMO levels were estimated from the tails of corresponding absorption spectra in solid state; the estimated values was 3.20 eV. This large energy gap suggests that the methyl groups bound to phenyl ring at 3-position disrupt effective π -conjugation between phenyl and thiophen ring. The low-lying HOMO energy level and wide band gaps suggest that **TTPT** compound might be a suitable host and hole blocking material in PHOLEDs.

To investigate the EL properties of **TTPT**, we fabricated a multilayer device. The layers of the device consist of ITO as the anode, CuPc as the hole injection layer, NPB as the hole-transporting layer, **TTPT**: 8%-Ir(piq)₃ as the emitter, BCP as the hole-blocking layer, Alq₃ as the electron transporting layer, LiF as the electron injection layer, and Al as the cathode (Fig. 3). We also fabricated another device as a reference device for comparison of EL efficiency. We chose *N,N'*-dicarbazolyl-4,4'-biphenyl (CBP) as the host and reference material, a prototypical host with a wide band gap for green or red OLEDs. In EL devices, red emission originated from Ir(piq)₃ was observed at 627 nm (λ_{\max}) with-

out any emissions from the host (Figure 4, inset). Moreover the EL spectra of these devices do not significantly change with variation of the applied voltage. The emission observed in the EL device supports the suggestion that complete energy transfer from the host to the dopant occurs at the 8 wt %-doped level.

The operating voltages (defined as 1 mA/cm²) of the **TTPT** based device and CBP based device are observed at 6.5 V and 5.5 V respectively. This observation implies that carrier injection occurs more effectively in CBP based device due to the fact that **TTPT** has the deeper HOMO energy (6.1 eV) than in CBP (5.7 eV).^{4,11}

The current density vs luminescence and current efficiency vs luminescence characteristics are depicted in Figure 4 and Figure 5, respectively. A maximum brightness of 7234 cd/m² at 10 V and luminance efficiency of 8.2 cd/A were achieved for **TTPT** based device, while a maximum brightness of 1962 cd/m² at 10 V and luminance efficiency of 5.8 cd/A were observed in CBP based device. These results illustrate that a **TTPT** based device shows higher efficiency than CBP based device, likely due to the bipolar character of **TTPT**, resulting in a broad recombination zone and well

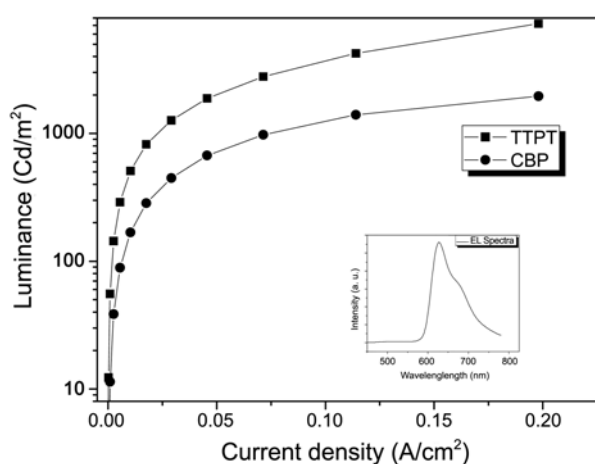


Figure 4. Current density vs luminance characteristics based on **TTPT** (squares) and **CBP** (circles). Inset: EL spectrum of **TTPT**.

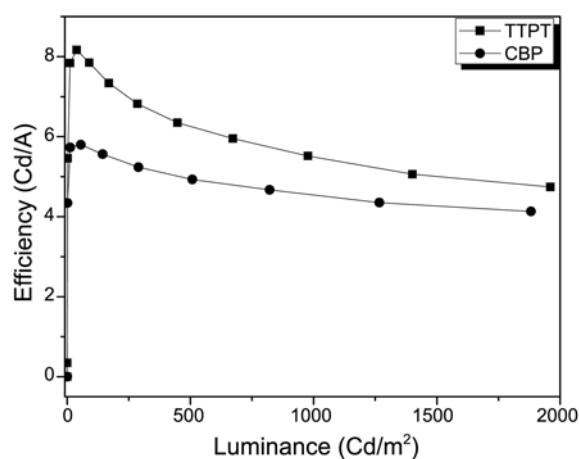


Figure 5. Luminance vs current efficiency characteristics based on **TTPT** (squares) and **CBP** (circles).

balanced transfer from charge to emissive layer.⁴

In summary, a triazine-based red host compound has been synthesized and characterized, including its thermal, photo-physical and electrochemical properties. The 1,3,5-phenyl-triazine core incorporated with thiophene or silyl segments can give rise to several distinct characteristics, impacting their electronic transition and photoluminescence, while thiophene substituent perturbed the absorption, redox potentials and EL efficiency. It also rendered bipolar character to **TTPT**. In particular, the low-lying HOMO in **TTPT** was observed, compared to that of **CBP**, indicating that the triazine core induced a relative diminution of the HOMO energy. Here, **TTPT**, was used as a host material exhibiting a bright emission in a multilayered PHOLED. Further improvement and optimization of EL devices fabricated by using these derivatives are currently being investigated in our laboratory.

Experimental Section

General Considerations. All experiments were performed under a dry N₂ atmosphere using standard Schlenk techniques. All solvents were freshly distilled over appropriate drying reagents prior to use unless otherwise stated. All starting materials were purchased from either Aldrich or Strem and used without further purification.

Synthesis of 2,4,6-Tris(3-methyl-4-(trimethylsilyl)phenyl)-1,3,5-triazine(TSPT). A solution of *n*-butyllithium (1.5 mL, 1.6 M solution in hexane, 7.35 mmol) was added dropwise to a solution of 2,4,6-tris(4-bromo-3-methylphenyl)-1,3,5-triazine (1.12 g, 2.04 mmol) in THF at -78 °C. The reaction mixture was maintained at this temperature for an additional 1 h, and then trimethylsilylchloride was slowly added. The reaction mixture was allowed to room temperature and stirred for 24 h. The reaction mixture was quenched with 2 N-HCl at 0 °C, and then extracted with CH₂Cl₂. Organic layers were sequentially washed with water, dried over MgSO₄, and then filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica column chromatography using CH₂Cl₂ and hexane (v/v:1:5) to give titled compounds (10-20% isolated yield) as a white solid. mp 210 °C. MS (EI): *m/z* = 552 [M]⁺. ¹H-NMR (CDCl₃, 300 MHz): δ 8.32-8.30 (m, 6H), 7.49 (m, 3H), 2.44 (s, 9H), 0.20 (s, 27H). ¹³C-NMR (CDCl₃, 100 MHz): δ 172.0, 144.1, 137.2, 134.9, 133.0, 131.1, 130.4, 129.7, 125.4, 23.375, 0.01.

Synthesis of 2,4,6-Tris(3-methyl-4-(thiophen-2-yl)phenyl)-1,3,5-triazine(TTPT). To a solution of 2,4,6-tris(4-bromo-3-methylphenyl)-1,3,5-triazine (1.12 g, 2.04 mmol) in THF (15 mL) was added dropwise a solution of *n*-butyllithium (1.5 mL, 1.6 M solution in hexane, 7.35 mmol) at -78 °C. The mixture was allowed to react at this temperature for 1 h. A solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.46 mL, 12.84 mmol) in THF (5 mL) was added dropwise to the cooled mixture. The mixture was allowed to warm to room temperature to react for 24 h. The reaction was quenched with 2 M-HCl at 0 °C. Ethylacetate was added into the mixture, and the organic

layer was separated, washed with brine, and dried with MgSO₄. The solvent was evaporated and the residue was purified by column chromatography on silica gel with CH₂Cl₂. Subsequently, isolated borate (4 g, 5.48 mmol) was dissolved in THF (20 mL). To a mixture of 2-bromothiophene (4.47 g, 27.42 mmol), 2 M-Na₂CO₃ (27.42 mL, 54.84 mmol) and Pd(PPh₃)₄ (0.25 g, 0.22 mmol) was added slowly a solution of above borate at room temperature. The mixture was stirred for 24 h at 65 °C, and was poured into water and ethylacetate. The solvent was removed under reduced pressure and sticky residue was purified by column chromatography. The isolated yield of title compound is 80-85%. (eluent; CH₂Cl₂:Hexane = 1:5(v/v), *R_f* = 0.3) MS (EI): *m/z* = 597 [M]⁺; ¹H-NMR (CDCl₃, 400 MHz): 8.63 (s, 3H), 8.59 (dd, *J* = 8.1, 1.4 Hz, 3H), 7.64 (d, *J* = 8.1 Hz, 3H), 7.42 (dd, *J* = 5.1, 1.0 Hz, 3H), 7.22 (m, 3H), 7.15 (m, 3H), 2.63 (s, 9H), ¹³C-NMR (CDCl₃, 100 MHz) δ 171.7, 143.0, 138.7, 136.5, 131.7, 127.8, 127.4, 127.0, 126.3, 22.1.

Acknowledgments. This work was supported by the Industrial strategic technology development program (10039141) funded by the Ministry of Knowledge Economy (MKE, Korea). Also this research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0010518).

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